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Ordered Moment of NiS_2*

Abstract: The transition metal dichalcogenides exhibit a wide variety of both electrical and magnetic properties, from insulators to superconductors and from ferromagnetism through antiferromagnetism to diamagnetism. NiS_2 is a semiconductor with an anomalous paramagnetic behavior which leaves in doubt the existence of a local moment. Previous neutron diffraction data have failed to show any ordering down to 4.2°K. Our neutron powder diffraction data on stoichiometric NiS_2 show a transition at 40°K to a structure which can be described as ordering of the first kind. This is followed by an abrupt transition at 30°K in which *additional* diffraction peaks appear and these are consistent with ordering of the second kind. Despite the fact that the powder data cannot indicate an unambiguous magnetic structure, the magnitude of the ordered moment can be fixed. The rms moments associated with ordering of the first and second kinds are 1.0 and 0.60 μ_B per nickel atom, respectively, and the total moment is 1.17 μ_B per nickel atom.

The transition metal dichalcogenides MX_2 (M = Mn, Fe, Co, Ni, Cu, Zn; X = S, Se, Te) crystallizing with the pyrite structure have all been synthesized[1] with the exception of $ZnTe_2$. In particular, the disulfides exhibit a wide variation in both electrical and magnetic properties, ranging from semiconductors to superconductors and from diamagnets to ferro- or antiferromagnets. NiS_2 is a semiconductor with an anomalous paramagnetic behavior which leaves in doubt the existence of a local magnetic moment.[1] A very recent neutron diffraction investigation[2] failed to find any evidence of ordering down to 4.2°K. Because of the continued interest in NiS_2 arising, in part, from the possibility that it may represent a Mott insulator, a further search for possible magnetic ordering using neutron diffraction was thought to be worthwhile.

A series of powder diffraction patterns was obtained using a carefully prepared sample[3] and these patterns indeed indicate a transition to an antiferromagnetic state. Figure 1 shows the pattern obtained at 4.2°K with the magnetic peaks labeled with the symbols M_1 or M_2. The indexing of the pattern is based on a cubic unit cell with the cell edge equal to $2a_0$, where the dimension of the chemical unit cell is $a_0 = 5.689$ Å. The points in Fig. 2 indicate the measured temperature dependence of the two sets of magnetic reflections M_1 and M_2, using the (111)M_2 and (200)M_1 as representative peaks. The curves shown in the figure were calculated using a Brillouin

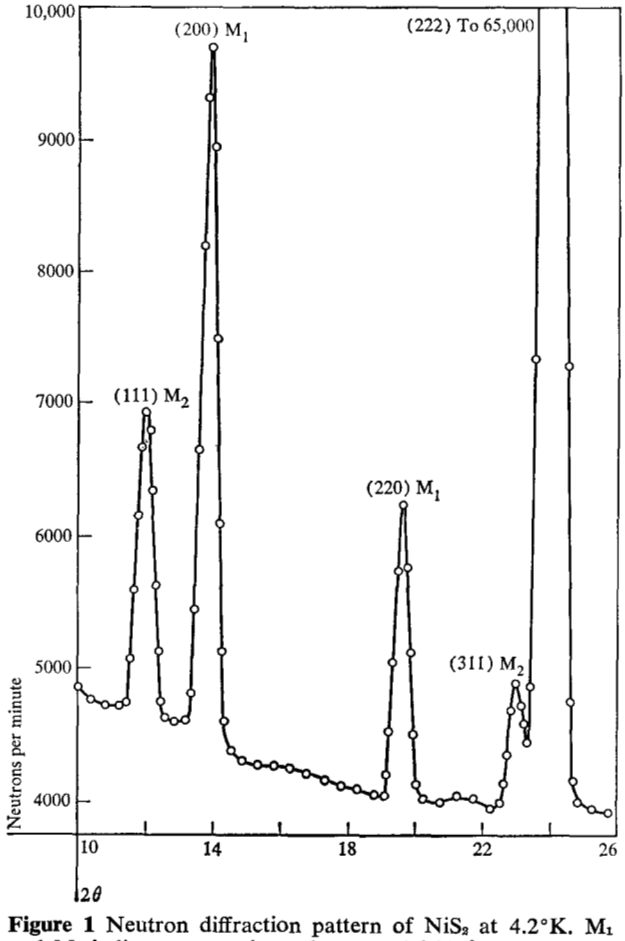

Figure 1 Neutron diffraction pattern of NiS_2 at 4.2°K. M_1 and M_2 indicate magnetic peaks. $\lambda = 1.364$ Å.

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* Work performed under the auspices of the U. S. Atomic Energy Commission.

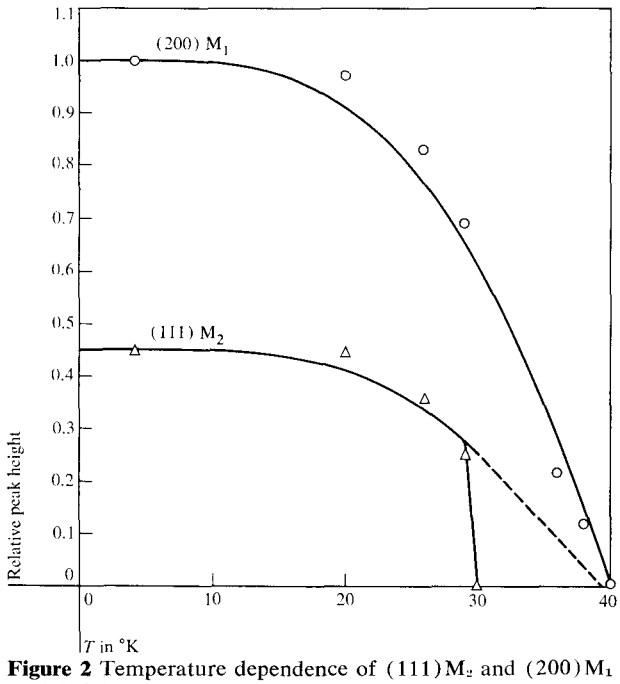

Figure 2 Temperature dependence of (111)M_2 and (200)M_1 peak heights.

function for spin 1/2, assuming a T_N of 40°K for the M_1 reflections and 39°K for the M_2. The (200)M_1 reflection appears to behave normally with a Néel temperature of about 40°K. The (111)M_2 reflection, in contrast, appears suddenly in the neighborhood of 30°K and over a very narrow temperature interval (<1°K) reaches an intensity consistent with an extrapolated Néel temperature which is also about 40°K. This behavior strongly suggests a first-order transition. On the other hand, the (200)M_1 is completely uninfluenced by the sudden appearance of the M_2 reflections, indicating that the M_1 and M_2 reflections are independent. The M_1 peaks are characterized by having all even indices, which means that they could have been indexed using the chemical unit cell. In the smaller cell, the indices are mixed and thus the M_1 reflections correspond to ordering of the first kind since the magnetic atoms lie on a fcc lattice. The M_2 peaks have all odd indices and can thus be associated with ordering of the second kind.

The procedure adopted in analyzing the data, based on the independence of the M_1 and M_2 reflections, was to treat the two sets separately in the most general terms and then attempt to combine them. For ordering of the first kind, the structure factors for a general non-collinear model with no restriction on the size of the individual spins can be shown to be $F^2_{200} = (4/3)[(\sum s_i^2/2) - A]$ and $F^2_{220} = (\sum s_i^2) + (2/3)\,A$. The symbol A represents a lengthy combination of products of spin components. The summation is over the spins, s_i, in the magnetic unit cell. Using the observed value of 2.0 for F^2_{200}/F^2_{220}, one finds that $A = -\sum s_i^2/2$, giving $F^2_{200} = (4/3)\sum s_i^2$ and $F^2_{220} = (2/3)\sum s_i^2$. Thus a measurement of F^2 yields a value of $\sum s_i^2$ and hence $\langle s_1^2 \rangle$ ($\langle \cdots \rangle$ represents average value) for the M_1 spins completely independent of any knowledge of the structure. An entirely analogous treatment is possible if one assumes ordering of the second kind for the M_2 reflections, that is that the spins alternate in sign along the three cube edges in going from one *chemical* unit cell to the next. Then one finds that $F^2_{111} = (2/3) \times 64\,[(\sum s_i^2) + B]$ and $F^2_{311} = (2/3) \times 64\,[(\sum s_i^2) - (5/11)\,B]$. In this case the summation is over only the spins in a *chemical* unit cell. As before, B is a combination of products of individual spin components. The observed value of the ratio F^2_{111}/F^2_{311} is 33.0/17.0 so that B equals $\sum s_i^2/2$, giving $F^2_{111} = 64\sum s_i^2$ and $F^2_{311} = (17/33) \times 64\sum s_i^2$. Thus, just as in the M_1 case, we can fix $\sum s_i^2$ and $\langle s^2 \rangle$ for the M_2 spins despite our lack of knowledge of an unambiguous structure.

Furthermore, the assumption that the M_2 peaks are associated with ordering of the second kind, i.e., that the spins alternate in sign along x, y and z, enables one to compute the average value $\langle s^2 \rangle$ per site of the square of the spin for the combined set. The assumption of ordering of the second kind is equivalent to making s_1 and s_2 completely independent so that $\langle s^2 \rangle = \langle (s_1 + s_2)^2 \rangle$ reduces to $\langle s_1^2 \rangle + \langle s_2^2 \rangle$. The results for NiS_2, based on the data taken at 4.2°K, are $\langle \mu_1 \rangle = 1.00\ \mu_B$, $\langle \mu_2 \rangle = 0.60\ \mu_B$ and $\langle \mu \rangle = 1.17\ \mu_B$ where μ is the moment. The average ordered moment per site of 1.17 μ_B is considerably less than expected on the basis of the observed paramagnetic moment, which indicated two unpaired electrons.

In addition, diffraction data were collected[3] on a sample of CoS_2 in order to see if the ordered ferromagnetic moment was indeed 0.84 μ_B as determined by means of magnetization measurements. The neutron diffraction data give a value of 0.85 μ_B in excellent agreement with the magnetization result.

References

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2. K. Adachi, K. Sato and M. Takeda, *J. Phys. Soc. Japan* **26**, 631 (1969).
3. The samples of NiS_2 and CoS_2 were prepared by R. J. Bouchard in a sealed silica tube. See Reference 1.

Received November 4, 1969